

CLAIMS

1. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

5		Carbon	0.01 – 0.7%
		Silicon	0.1 – 3.0%
		Manganese	0 – 2.5%
		Nickel	15 – 90%
10		Chromium	5 – 40%
		Molybdenum	0 – 3.0%
		Niobium	0 – 2.0%
		Tantalum	0 – 2.0%
		Titanium	0 – 2.0%
15		Zirconium	0 – 2.0%
		Cobalt	0 – 2.0%
		Tungsten	0 – 4.0%
		Hafnium	0.01 – 4.5%
		Aluminium	0 – 15%
20		Nitrogen	0.001 – 0.5%
		Oxygen	0.001 – 0.7%
		balance iron and incidental impurities,	

with the proviso, that at least one carbide forming element whose carbide is more stable than chromium carbide selected from niobium, titanium, tungsten, tantalum and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

2. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

Carbon	0.01 to 0.5%
Silicon	0.01 to 2.5%

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	Manganese	0 to 2.5%
	Nickel	15 to 50%
	Chromium	20 to 40%
	Molybdenum	0 to 1.0%
5	Niobium	0 to 1.7%
	Titanium	0 to 0.5%
	Zirconium	0 to 0.5%
	Cobalt	0 to 2.0%
	Tungsten	0 to 1.0%
10	Hafnium	0.01 to 4.5%,

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is
15 present and that at least part of the hafnium is present as finely divided oxide
particles.

3. An alloy according to claim 1 having the following composition, by
weight:

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	Carbon	0.3 to 0.7%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	30 to 40%
25	Chromium	20 to 30%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
30	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.
	Nitrogen	0.001 – 0.5%

Oxygen 0.001 – 0.7%
Balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is
5 present and that at least part of the hafnium is present as finely divided oxide
particles.

4. An alloy according to claim 1 having the following composition, by
weight:

10	Carbon	0.03 to 0.2%
	Silicon	0.1 to 0.25%
	Manganese	2.5% max.
	Nickel	30 to 40%
15	Chromium	20 to 30%
	Molybdenum	3.0% max.
	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
20	Zirconium	0.5% max.
	Cobalt	2.05% max.
	Tungsten	1.0% max.
	Aluminium	0 – 15.0%
	Nitrogen	0.001 – 0.5%
25	Oxygen	0.001 – 0.7%
	balance iron and incidental impurities,	

with the proviso that at least one of niobium, titanium and zirconium is
present and that at least part of the hafnium is present as finely divided oxide
30 particles.

5. An alloy according to claim 1 having the following composition, by
weight:

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	Carbon	0.3 to 0.7%
	Silicon	0.01 to 2.5%
	Manganese	2.5% max.
5	Nickel	40 to 60%
	Chromium	30 to 40%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
10	Titanium	1.0% max.
	Zirconium	1.0% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Aluminium	0 – 15.0%
15	Nitrogen	0.001 – 0.5%
	Oxygen	0.001 – 0.7%

balance iron and incidental impurities,

20 with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

6. An alloy according to claim 1 having the following composition, by weight:

25	Carbon	0.03 to 0.2%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	40 to 50%
30	Chromium	30 to 40%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%

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	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.,
5	Aluminium	0 – 15.0%
	Nitrogen	0.001 – 0.5%
	Oxygen	0.001 – 0.7%
	balance iron and incidental impurities,	

10 with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

15 7. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.3 to 0.7%
	Silicon	0.01 to 2.5%
	Manganese	2.5% max.
20	Nickel	19 to 22%
	Chromium	24 to 27%
	Molybdenum	3.0% max.
	Niobium	2.0% max
	Hafnium	0.01 to 4.5%
25	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Aluminium	0 – 15.0%
	Nitrogen	0.001 – 0.5%
	Oxygen	0.001 – 0.7%
30	balance iron and incidental impurities,	

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide

particles.

8. An alloy according to claim 1 having the following composition, by weight:

5		Carbon	0.03 to 0.2%
		Silicon	0.1 to 2.5%
		Manganese	2.5% max
		Nickel	30 to 45%
10		Chromium	19 to 22%
		Molybdenum	3.0% max.
		Niobium	2.0% max.
		Hafnium	0.01 to 4.5%
		Titanium	0.5% max.
15		Zirconium	0.5% max.
		Cobalt	2.0% max.
		Tungsten	1.0% max.
		Aluminium	0 – 15.0%
		Nitrogen	0.001 – 0.5%
20		Oxygen	0.001 – 0.7%
		balance iron and incidental impurities,	

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

9. An alloy according to any one of claims 1, 2, 3, 5, or 7, having a carbon content of from 0.3 to 0.5% by weight.

10. An alloy according to claim 1 or 2, having a carbon content of from 0.03 to 0.2% by weight.

11. An alloy according to claim 1, in which the amount of carbon in the

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alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.

12. An alloy according to claim 11, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.

13. An alloy according to claim 11 or 12, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.

14. An alloy according to any one of the preceding claims, in which the amount of carbon in the alloy, by weight, is from 0.03 to 0.2% and the amount of hafnium in the alloy, by weight, is from 1 to 4.5%.

15. An alloy according to any one of claims 1 and 4 to 8, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 10% and the amount of hafnium by weight is from 0.01% to 4.5%.

16. An alloy according to claim 15, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 6% and the amount of hafnium by weight is from 0.1% to 1.0%.

17. An alloy according to claim 15 or 16, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 4.5% and the amount of hafnium by weight is from 0.2% to 0.5%.

18. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less.

19. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles

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having an average particle size of from 5 microns to 0.25 microns, or less.

20. An alloy having any one of the following compositions, by weight:

5	Carbon	0.45%
	Silicon	1.3%
	Manganese	0.9%
	Nickel	33.8%
	Chromium	25.7%
10	Molybdenum	0.03%
	Niobium	0.85%
	Hafnium	0.25%
	Titanium	0.1%
	Zirconium	0.01%
15	Cobalt	0.04%
	Tungsten	0.01%
	Nitrogen	0.1%
	Iron	balance,

20 with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

25	Carbon	0.07%
	Silicon	1.0%
	Manganese	0.98%
	Nickel	32.5%
	Chromium	25.8%
30	Molybdenum	0.20%
	Niobium	0.04%
	Hafnium	1.1%
	Titanium	0.12%
	Zirconium	0.01%

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Cobalt	0.04%
Tungsten	0.08%
Nitrogen	0.1%
Iron	balance,

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with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

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Carbon	0.34%
Silicon	1.68%
Manganese	1.10%
Nickel	32.0%
Chromium	21.3%
Molybdenum	0.01%
Niobium	0.80%
Hafnium	0.25%
Titanium	0.12%
Zirconium	0.01%
Aluminium	3.28%
Cobalt	0.04%
Tungsten	0.01%
Iron	balance,

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with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

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Carbon	0.42%
Silicon	1.79%
Manganese	1.17%
Nickel	33.2%

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	Chromium	23.3%
	Molybdenum	0.02%
	Niobium	0.77%
	Hafnium	0.24%
5	Titanium	0.10%
	Zirconium	0.01%
	Aluminium	1.64%
	Cobalt	0.04%
	Tungsten	0.08%
10	Iron	balance,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

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21. An alloy according to any one of the preceding claims substantially as described in Examples 1 to 4.

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22. An alloy according to any one of the preceding claims substantially as described in Example 5.

23. A nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

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24. An oxide dispersion strengthened nickel-chromium-iron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely divided oxidised particles.

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25. A corrosion resistant nickel-chromium-iron-aluminium alloy comprising up to about 15%, preferably up to about 10%, by weight, of aluminium and up to about 5% by weight of hafnium-containing particles.

26. A method of manufacturing an oxide dispersion strengthened

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nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

5 27. A method according to claim 26, in which the alloy is an alloy as claimed in any of claims 1 to 25.

28. A method according to claim 26 or 27, wherein the hafnium particles have a particle size of less than 50 microns.

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29. A method according to any one of claims 26 to 28, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.

30. A method according to any one of claims 26 to 29, wherein the
15 hafnium particles are added to the melt shortly before pouring the molten alloy into a mould.

31. A method according to claim 30, in which the hafnium particles are added to the molten alloy in a ladle.

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32. A method according to claim 30, in which the hafnium particles are added to the molten alloy in the furnace

33. A method according to anyone of claims 26 to 32, in which the
25 hafnium is electrolytic hafnium.

34. A method according to any one of claims 26 to 33, wherein the level of oxygen in the melt is varied by the addition of one or more substance selected from the group:

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silicon,
chromium,
manganese,
calcium,

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CaSi,
CaSiMn,
niobium,
titanium,
5 zirconium.

35. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and varying the level of oxygen in the melt by,
10 the addition of at least one substance chosen from the group:

silicon,
chromium,
manganese,
calcium,
15 CaSi,
CaSiMn,
niobium,
titanium,
zirconium.

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36. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that the formation of detrimental oxide from the reactive elements titanium, zirconium,
25 aluminium is reduced.

37. A method according to any one of claims 26 to 36 wherein any one of the elements titanium, zirconium or aluminium are added after hafnium into the melt.

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38. A method as claimed in claim 37 wherein any one of the elements titanium, zirconium or aluminium are added after the hafnium in the melt, and just before pouring in the mould.

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39. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which controls the partial pressure of oxygen to permit the oxidation of the hafnium in situ.

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40. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which controls the free oxygen content to permit the oxidation of the hafnium in situ.

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41. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which controls the partial pressure of at least one element selected from the following group:

15

oxygen,
carbon,
nitrogen,
hydrogen;

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to permit the oxidation of the hafnium in situ.

42. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which permits the oxidation in situ of beneficial oxide dispersion as hafnium oxide, avoiding the formation of detrimental precipitates.

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43. A method as claimed in claim 42 which limits in situ oxidation to beneficial oxide dispersion of hafnium oxides and avoid its reaction with slag.

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44. A method according anyone of claims 34 to 43, in which titanium is added in the form of TiFe after the hafnium addition.

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45. A method according to any of claims 26 to 44, in which the melt temperature is in the range of from 1350°C to 1700°C.

5 46. A method of manufacturing a corrosion resistant nickel-chromium-iron which comprises adding sequentially finely divided hafnium particles and aluminium to a melt of the alloy before pouring.

10 47. A method according to claim 46, wherein the aluminium is added to the melt immediately before pouring the molten alloy into a mould.

48. A method according to any one of claims 26 to 47, in which the alloy is formed into a tube by rotational moulding.

15 49. A method according to any one of claims 26 to 48 substantially as described in Examples 1 to 4.

20 50. A method according to any one of claims 26 to 49 substantially as described in Example 5.

51. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium particles to the melt before pouring.

25 52. A creep resistant alloy tube formed from a nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

53. A tube according to claim 52, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.

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54. A nickel-chromium-iron alloy tube comprising up to about 5% of hafnium-containing particles substantially as herein before described.

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55. A tube formed from an alloy according to any of claims 1 to 25 by rotational moulding.

56. A nickel-chromium-iron alloy having a structure and composition
5 substantially as described and illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.

57. A nickel-chromium-iron alloy having a structure substantially as
10 described and illustrated in Figures 5 or 6 of the accompanying Drawings.

58. A corrosion resistant alloy tube formed from a nickel-chromium-iron alloy comprising up to about 15% of aluminium and up to about 4.5% of hafnium-containing particles.

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59. A tube according to claim 58, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.

60. A tube formed from an alloy according to any of claims 1 to 25 by rotational moulding.

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61. An alloy according to any one of claims 1 to 25, 56 and 57 produced by a method according to any one of claims 26 to 51.

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